The Origin of Manganese Nodules: A Combined Theory with Special Reference to Palagonitization[1]

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ABSTRACT: Manganese responsible for nodular development is derived from both the oceans and the continents. The bulk of manganese is probably derived through continental weathering. Ferruginous compounds are incorporated into ocean-bottom sediment layers through submarine volcanism. Terrigenous manganese accretes by the catalytic action (or possibly a redox reaction) of iron and ferromanganiferous complexes present at the sediment-water interface. This results in the formation of manganese nodules which are at once the products of both normal continental and normal oceanic weathering. The rate of manganese accretion is partially dependent upon the rate of diagenetic palagonitization. New measurements indicate linear manganese accretion rates range from 1.7 to 8.7 mm/10^6 years. Rates for volumetric manganese accretion range from 110 to 1,300 $mm^3/10^6$ years. Initial development proceeds at the more rapid rate and subsequent accretion at the slower rate. Manganese nodules with centers other than volcanic debris (shark's tooth centers) may be formed as a result of related catalytic mechanisms.

TWO DISTINCT SCHOOLS of thought exist concerning the origin of manganese nodules. One group (Barnes and Dymond, 1967; Bender, Ku, and Broecker, 1966; Goldberg and Arrhenius, 1958; Kuenen, 1950) presents evidence to show that manganese is provided to the ocean system via continental weathering. The other group (Bostrom and Peterson, 1966; Bonatti and Nayudu, 1965; Lynn and Bonatti, 1965; Krauskopf, 1957) believes that the manganese is introduced via submarine volcanism. The process of terrigenous decomposition may be combined with the process of oceanic weathering to account for nodular manganese development. Manganese is derived mainly as a product of continental weathering, and then combines with ferruginous and ferromanganiferous complexes, produced as a by-product of submarine volcanism, to form manganese nodules. The argument presented is a modification of one proposed by Goldberg and Arrhenius in 1958.

Manganese is present in seawater in divalent form and is oxidized to tetravalent form under a catalytic action of iron hydroxides (Goldberg and Arrhenius, 1958) and ferromanganiferous complexes (Krauskopf, 1957). The reaction occurs at the sediment-water interface where tetravalent manganese is found (Goldberg and Arrhenius, 1958). It is not certain whether the process is a true catalysis or simply an oxidation-reduction reaction. The length of exposure of the sediment surface is related to the quantity of manganese deposited (Krauskopf, 1957). The longer the interval of time before burial of the sediment-water interface, the more manganese will be deposited on that interface. Manganese is transported into the ocean in an ionic divalent form rather than as a colloid attached to pelagic clays (Murata, 1939), although the possibility exists that both mechanisms are active. In either case, the tetravalent manganese concentration in the oceans is relatively constant. Our argument is based on the reported slow rate of manganese accretion as determined by our hydration dating and radio-

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metric dating (Barnes and Dymond, 1967; Bender, Ku, and Broecker, 1966; Ku and Broecker, 1963) compared to the faster rates of pelagic sedimentation.

Iron oxides, hydroxides, ferruginous manganese complexes, and associated heavy metals found in the manganese nodules evolve from the diagenetic solution of palagonite (Morgenstein, 1967; Bonatti and Nayudu, 1965). The release of iron from palagonite involves hydrolytic reactions in an oxidizing environment which are dependent upon Eh conditions (Morgenstein, 1967).

Much data have been presented concerning the rate of manganese accretion (Bender, Ku, and Broecker, 1966; Barnes and Dymond, 1967). In accord with the theory proposed by Goldberg and Arrhenius (1958), the quantity and rate of manganese accretion is dependent upon the time before burial by pelagic sediments and the rate of availability of a catalytic agent. We suggest that the catalytic agents (both iron and ferromanganese complexes) are derived through the process of palagonitization (Morgenstein, 1967). Hydrothermal solutions must also be of some importance (Bostrom and Peterson, 1966). Palagonite formation occurs both syngenetically and diagenetically, with the latter being the more important process.

Support for diagenetic palagonitization comes from our recent petrographic studies on palagonites from the Pacific, Atlantic, and Indian oceans (Figs. 1 and 2). The analyses have shown palagonite occurring along syngenetic and diagenetic fractures in sideromelane. In most cases the palagonite postdates the fractures. Fractures show both shear and tensile displacements, with the latter being more prevalent. The tensile fractures are similar to patterned mud cracks in that they occur with orthogonal connections. Furthermore, an immobile product layer (50 microns thick) between

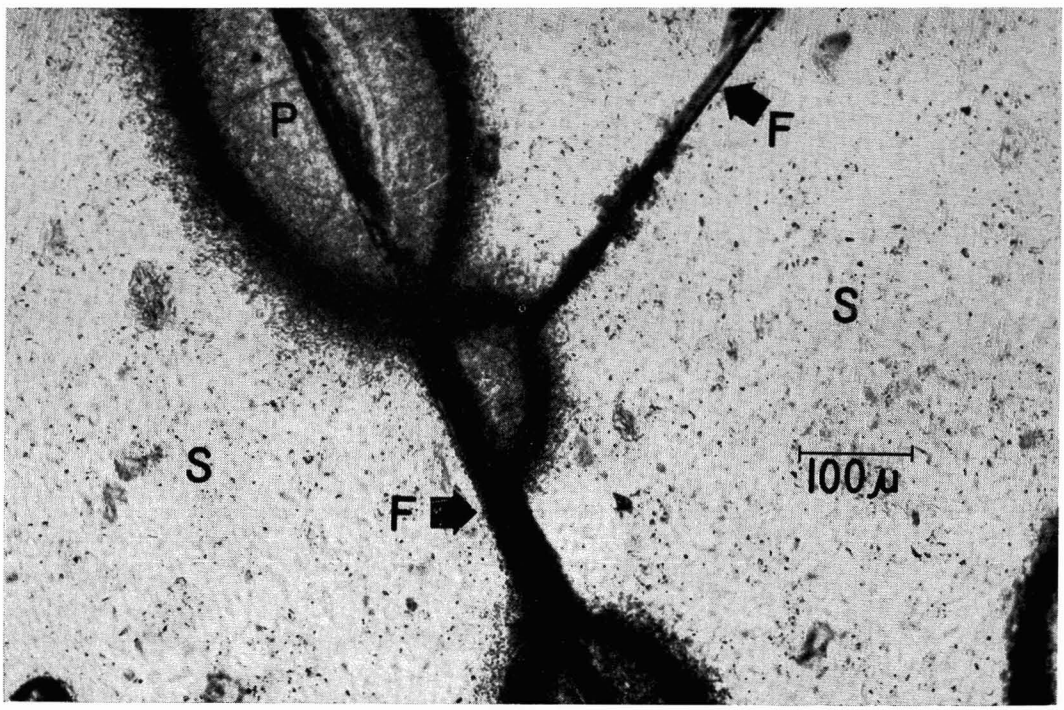

FIG. 1. Fractures (F) in sideromelane glass (S) with palagonite alterations (P) along the cracks. Microchannels and solid solution border separates the palagonite from the sideromelane. Diagenetic movements along the fractures are shown by apparent displacements of the palagonite alterations on either side of fractures in other photographs of this same sample. (Scale as shown, plane polarized light.) Lamont-Doherty Geological Observatory's Core V22-227, 69 cm.

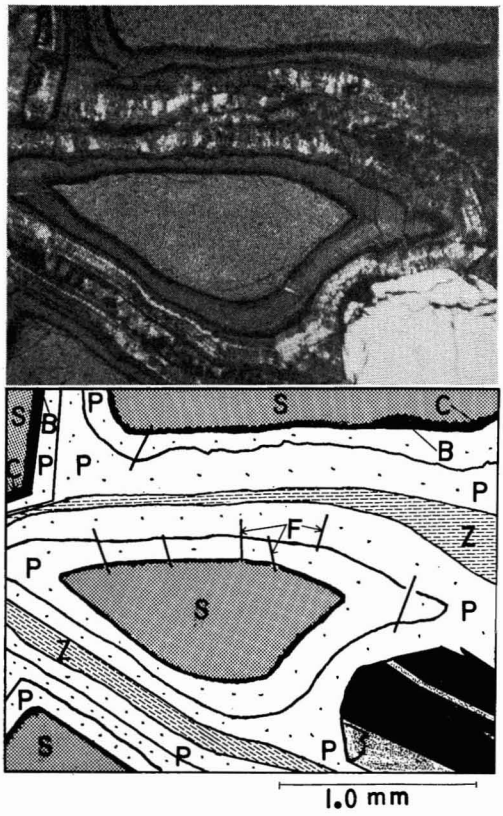

FIG. 2. Palagonite alteration of sideromelane. The grain centers are sideromelane (S). They are bordered by microchannels (C) and solid-solution borders (B) which separate them from bands of palagonite (P). Fractures (F) are present perpendicular to the palagonite banding. Each "cell" of sideromelane-palagonite is separated from its neighbor by voids (large fractures), here filled with zeolites, smectites, and ferruginous compounds (Z). (Scale as shown. Crossed nicols, gypsum plate. A calcic-plagioclase lath at right.) Mid-Atlantic ridge, Lamont-Doherty Geological Observatory's Core V25-12-T3.

palagonite and mafic volcanic glass has the configuration of microchannels through which seawater is carried into the basaltic glass. These microchannels are also observed in the remnant palagonite (Fig. 2). Typical palagonite banding is directly related to the microchanneling because the length of the channels approximates the average thickness of the bands (Morgenstein, 1969). Each band is separated from the other by a solid solution border which is enriched with ferromanganese oxides and hydroxides. This evidence indicates that diagenetic palagonitization as a producer of iron is more important than its syngenetic counterpart. (Further evidence for diagenetic palagonitization will be the subject of a forthcoming publication).

The significance of diagenetic palagonitization is in its role as a governor in controlling the rate of supply of ferruginous oxides to the sediment-water interface. The process of palagonite formation (glass hydration) involves a geometric volume increase which is caused by the addition of seawater to mafic volcanic glass. This volume increase is the cause of the fracturing cited above. As more palagonite is formed, more fracturing occurs. This results in a progressively increasing rate of iron and ferromanganese introduction into the sediment due to increase in surface area of the fracture. The nodule increases its surface area as it increases in volume, and demands ever-increasing amounts of iron and ferromanganese (via palagonitization) to maintain this growth. However, a point is eventually reached where (1) there is no more palagonite (i.e., it has all been "crystallized" to amorphous iron oxides), or (2) the nodule is being covered by sediment and is progressively farther removed from the manganese of seawater, or both. In any case the rate of growth diminishes after a brief initial surge.

Rates of manganese accretion, based on radiometric dating, are presented in Table 1. They range from 0.5 mm/10^6 years to 3.5 mm/10^6 years. Recent work by Morgenstein (1969) indicates a rate of diagenetic palagonitization in deep-sea volcanic sediments in the range of 2.0 mm/10^6 years to 3.5 mm/10^6 years. These rates were determined by measuring the thickness of palagonite in samples with known ages derived through paleontological investigations, and of known dates of volcanic flows. It is likely that some of the higher rates of manganese accretion are due to the upward migration and addition of this element and associated metals in a sediment column (Lynn and Bonatti, 1965), hydrothermal palagonite solution at depth serving as the direct source of the elements.

Recently, Rossmann and Callender (1968) described the occurrence of ferromanganese nodules in Lake Michigan and suggested that

TABLE 1

RATES OF MANGANESE ACCRETION

AUTHOR	MANGANESE RATE RANGE, mm/10^6 YEARS	METHOD
Ku and Broecker (1963)	4.0 to 4.3	Th, Pa, U
Bender, Ku, and Broecker (1966)	2.5 to 3.0	Th
Barnes and Dymond (1967)	0.5 to 3.5	K:Ar
	6.0 to 18.0	Th
	24.0 to 40.0	U
Morgenstein (1969)	1.7 to 8.7	devitrification of sideromelane

the metals are derived via drainage of the extensive ore deposits in the vicinity of the lake. The availability of iron complexes suggests the possibility that catalytic mechanisms similar to those of the ocean environment may be responsible for nodular development in the lacustrine environment. A comparison of Mn:Fe ratios in both environments is shown in Table 2. The close agreement of Mn:Fe values for Lake Michigan, Atlantic Ocean, and Pacific Ocean nodules partially supports the above suggestion.

TABLE 2

MANGANESE:IRON RATIOS

Mn:Fe	AREA	SOURCE
0.15	Lake Michigan (minimum value)	Rossmann and Callender (1968)
		Rossmann and Callender (1968)*
1.47	Lake Michigan (maximum value)	Rossmann and Callender (1968)*
0.75	Lake Michigan (average value)	Rossmann and Callender (1968)
1.73	Pacific Ocean (average value)	Arrhenius (1963)
		Arrhenius (1963)*
0.93	Atlantic Ocean (average value)	Arrhenius (1963)*

* Mn:Fe ratio calculated from data presented by these authors.

Most lacustrine nodules, however, are richer in Fe than Mn and thus accumulation rates are much faster in lakes than in oceans. It is obvious that palagonite control of the rate of iron formation is not applicable in the Lake Michigan case. It is not surprising that relatively large (0.5 to 30.0 mm in diameter) nodules were reported by Rossmann and Callender (1968) indicating, as they do, a much higher rate of nodular development during the geologically short history of Lake Michigan. The proximity of the great iron-ore deposits in this area provide an immediate and abundant source of iron to the lake. Perhaps of even more significance quantitatively is the fact that large portions of Lake Michigan, particularly Green Bay, are presently in the throes of extensive biological and industrial pollution, a product of which is the precipitation and concentration of iron.

It is perhaps not too farfetched at this point to suggest the possibility of establishing manganese "farms" by "planting" iron-rich debris (such as junked cars) on the shallow seabed in restricted coastal areas, and then returning in a relatively short time to "harvest" the manganese crusts and nodules accreted about the "seeds." This has already been accidently accomplished. Goldberg and Arrhenius (1958) reported the recovery of a manganese nodule in the San Clemente Basin. The "seed" of the nodule is a spent bombshell dropped within this century when the San Clemente Basin was a target range. Extrapolated rates indicated nodular development in the range of 1,000,000 mm/10^6 years.

This suggestion of future economic exploitation would become more palatable if there were a plausible explanation for the variation of manganese accretion rates. Table 3 and Figure 3 report rates of radial manganese growth as a function of total age of samples studied. There is a paucity of published information reporting both the rates of accretion and the total sample age. However, based upon 17 samples, the preliminary conclusion is drawn that radial manganese growth rates decrease with time. Table 4 reports rates of volumetric manganese accretion as a function of total age of nodules from a single dredge V16-SBT3. Again, the volumetric rate of manganese accretion decreases

with increasing age of the samples as computed for whole nodules of different ages. Reasons for this decrease have been explained earlier, and are probably a function of the decrease of the iron catalyst supply as well as removal of the nodule from the terrestrial manganese supply by burial during pelagic sedimentation. The concept that iron catalytic supply controls the formation rate of manganese nodules is supported by the decreasing rates of accretion of these nodules with time. The entire argument is based upon these observations (Fig. 3, and Tables 3 and 4). It is concluded from our previous arguments that:

TABLE 3

MANGANESE ACCRETION RATES AND THEIR RESPECTIVE AGES

SAMPLE	LOCATION	AGE BASED ON MEAN PALAGONITE RATES, 10^6 YEARS	Mn THICKNESS, mm	Mn RATE, mm/10^6 YEARS
V16-SBT3	lat. 13°04′ S long. 24°41′ W			
A		0.7	6	8.58
B		0.8	6	7.50
C		1.2	5	4.17
D		1.2	4	3.33
E		1.0	5	5.00
F		0.7	5	7.14
G		0.7	5	7.14
H		0.5	4	8.00
I		1.2	5	4.17
V16-130	lat. 59°23′ S long. 132°46′ W			
A		1.7	10	5.88
B		1.4	11	7.86
A150-RD8	lat. 31°49′ N long. 42°25′ W	14.5	30	2.07
V22-227	lat. 30°23′ N long. 47°14′ W	4.1	7	1.71

SAMPLE*	METHOD OF DATING*	AGE BASED ON RADIOGENIC DECAY,* 10^6 YEARS	Mn THICKNESS**	Mn RATE,* mm/10^6 YEARS
DWHD47	K:Ar (anor.)	9.8 ± 0.2	—	0.5–1.0
DWHD47	K:Ar (amph.)	9.3 ± 0.3	—	0.5–1.0
Horizon	K:Ar (plag.)	28.9 ± 1.4	—	2.0–3.0
Fan BD20	K:Ar (glass)	2.0 ± 0.3	—	2.6–3.5

* Barnes and Dymond (1967), Table 1, page 1218.
** Not reported by above authors.

TABLE 4

VOLUMETRIC MANGANESE ACCRETION RATES AND THEIR RESPECTIVE AGES FOR DREDGE V16-SBT3

V16-SBT3	AGE, $\pm.3 \times 10^6$ YEARS	RADIUS, mm	VOLUME $(4/3\pi R^3)$, mm^3	RATE, mm^3/10^6 YEARS
D	1.2	4	268.07	223.46
C	1.2	5	523.75	436.46
I	1.2	5	523.75	436.46
E	1.0	5	523.75	523.75
H	0.5	4	268.16	536.32
F	0.7	5	523.75	748.21
G	0.7	5	523.75	748.21
B	0.8	6	905.04	1,131.30
A	0.7	6	905.04	1,292.91

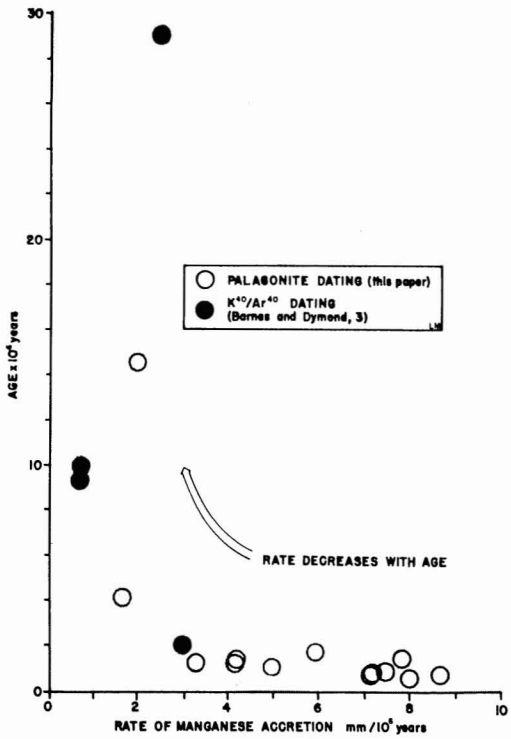

FIG. 3. Manganese accretion rates versus age of sample. Dating of 17 samples using the K:Ar and palagonite methods. Strippled area, showing manganese accretion rates decreasing with age, reflects a wide range of variation due to limited data. Nonetheless, it is apparent that the rate of manganese accretion decreases with the age of the sample.

1. If the supply of an iron catalyst, as well as its rate of reaction, can be controlled, then the rate of manganese nodular development can be regulated.

2. There exist differential accretion rates for manganese through time. This supports our contention that a major controlling factor for manganese growth (whether as crusts or nodules) is the availability of associated catalytic agents, mainly iron. Of course, the possibility also exists that there is a variation of the manganese supply from the continents. We do not believe that this is the case, because there is no reason to believe that the components derived from continental weathering should vary to any great extent during the relatively short period of geologic time dealt with in this paper.

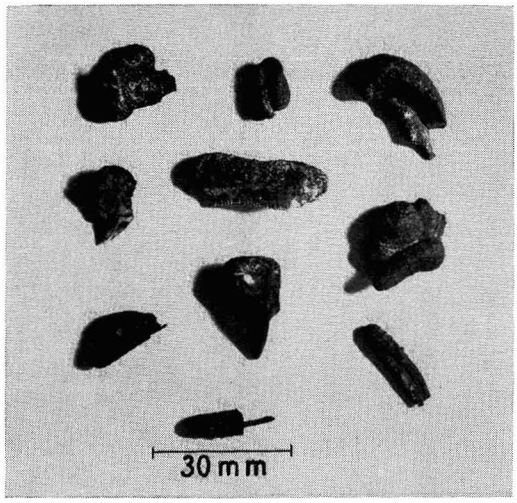

FIG. 4. Manganese nodules with shark's tooth and phosphatic bone centers. Lamont-Doherty Geological Observatory's dredge V16-SBT3 is from the South Atlantic Ocean. In the same dredge trawl most manganese nodules recovered contained palagonite centers. (Scale as shown.)

3. If all the constituents in manganese nodules were derived from submarine volcanism then manganese nodules would only be associated with volcanic materials and not with normal pelagic sediments. In some instances it can be shown that biologic conditions may substitute for volcanic conditions in providing iron (probably as in Lake Michigan), or possibly, as several authors (Krauskopf, 1957) have suggested, manganese itself may act as its own catalyst. In many cases a purely biotic transfer mechanism (bacterial action) acts as a catalytic agent for manganese accretion in both lakes and oceans (Krauskopf, 1957). In other instances it can be shown that phosphate acts as a catalyst for iron precipitation. Once the iron is in the sediment it acts as a catalytic agent for nodular manganese development. Examples are shown in Figure 4 with shark's tooth and other phosphate-rich debris forming the centers of the manganese nodules, instead of the more common volcanic particles. It would be most difficult to explain these occurrences by submarine volcanism.

In the ocean system, then, iron and associated catalytic agents originate through the solution of

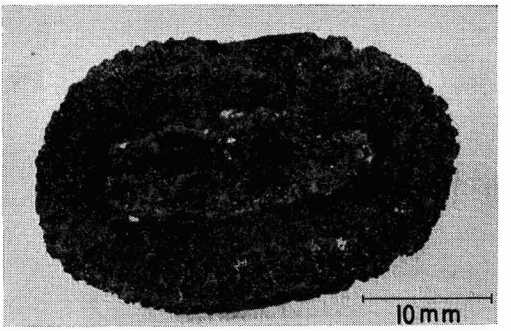

FIG. 5. Manganese nodule with sideromelane and palagonite center. The sample, Lamont-Doherty Geological Observatory's Core V16-130, is from the Bellingsshausen Basin, South Pacific. (Scale as shown.)

decomposition products (palagonite) of submarine volcanic glass. The bulk of the manganese is derived from terrestrial sources and then reacts with these authigenetic iron and ferromanganese complexes. This explains the association of manganese and volcanic material (Fig. 5), and, at the same time, accounts for the relatively slow rate of accretion of the nodules (due to a terrigenous manganese source). The rate of manganese accretion in many cases depends ultimately upon the rate of diagenetic palagonitization because the decomposition of palagonite provides the necessary catalytic agents such as iron and ferromanganese complexes for manganese nodular development.

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